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Physical ageing study of post-treated pim-1 membranes: Effect on gas transport properties

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PIM-1 is a glassy polymer of the class of the polymers with intrinsic microporosity (PIMs) which possess unique molecular structures resulting in a high free-volume. PIM-1 membranes combine very high gas permeability with a solubility controlled permeation [1, 2], its performance is close to or on Robeson's upper bound [3] for important gas pairs (*e.g.*, O_2/N_2, CO_2/CH_4) [4]. However, these membranes are very sensitive to the preparation protocol.

Glassy polymers lose excess free volume over time. This process, referred to as physical aging, generally reduces gas permeability and increases selectivity, particularly in the thin films applied to gas separation systems [5]. Purpose of this work is to gain a deep insight in the physical aging of self-supported and composite PIM-1 films.

The influence of alcohol and thermal treatment on the behaviour of PIM-1 dense films will be discussed, elucidating the various factors influencing the aging phenomena, as well as the effect of the aging on sorption, permeation and free volume. Composite membranes comprising a thinner polymer layer on a porous support were also studied and reveal much faster aging than thick films.

Dense films were prepared by solvent evaporation, wile composite membranes were obtained via solution casting technique. The membranes were tested as prepared and then treated under different protocols. Soaking of the membranes with alcohol was used to cancel the previous history of the samples and to remove residual solvent. A thermal treatment was subsequently carried out in the range of 25 to 125 °C.

Permeation tests were carried out for six permanent gases (H_2, He, CH_4, O_2, N_2 and CO_2) according to the time lag method. Sorption tests were independently carried out, using a McBain quartz spring balance.

Permeability of all films decreases with aging time, consistent with a loss of fractional free volume. In particular, the diffusion coefficient is reduced over time, while the selectivity is slightly enhanced.

The thermal treatment results in a faster permeability reduction and in an increased gas solubility. Some representative results in terms of carbon dioxide permeability are reported in Figure 1 for films treated according to different protocols. The sample treated at 125 °C seems to be more stable against aging in the long term, but has a lower initial permeability due to accelerated aging by the heat treatment.

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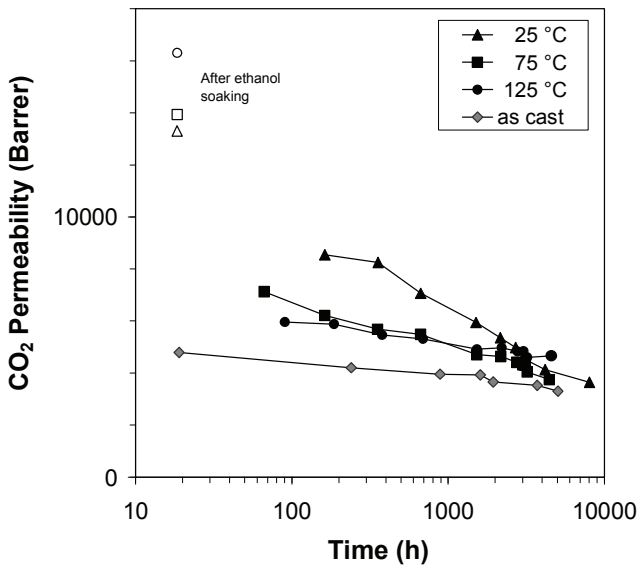

Figure 1. Carbon dioxide permeability in PIM-1 films tracked over time after different membrane conditioning protocols.

Carbon dioxide sorption isotherms are well described by the dual mode sorption model with a fairly good correspondence between the indirect estimation of the solubility coefficient from permeation tests and the values obtained from a sorption balance.

Strategies to reduce time dependency of such high free-volume materials will be proposed as well.

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